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F centre density in quenched KCl crystals

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F band absorptions have been measured in KCl crystals before and after quenching in different media. The concentration of *F* centres increases upon quenching and the increase is more for faster quenches. It is also higher in the outer region compared to the interior of the quenched crystal. These results have been explained in terms of strains and other defects produced by quenching

1 Introduction

The concentration of *F* centres formed by X-radiation in KCl crystal depends very much on the nature and concentration of impurity ions, stresses and strains present in the crystal prior to irradiation (Schulman & Compton 1962). Quenching from high temperature also increases the *F* centre density in the crystal. This has been explained to be due to the increase in dislocations which are the sources of vacancies for the formation of *F* centres (Seitz 1954) From the measurement of the change in hardness produced by quenching Kear & Pratt (1959) have shown that thermally produced vacancies associate forming pairs and later clusters during faster quench whereas slower quenching rates may permit redistribution of vacancy pairs within the clustdrs leading to the formation of dislocations. Further, quenching also produces a decrease in the sizes of the crystallites constituting the big crystal which amounts to increasing defects like grainboundaries and internal cracks (Parker & Schneider 1956). In order to correlate the increase of *F* centres and the defects produced upon quenching, it is necessary to have measurements on *F* band for different rate of quenching. Crystals were heated in air at 750°C for two hours and were quenched in carbon tetrachloride and air. Some crystals were also slowly cooled from the same temperature at the rate of 4°C/min. Since quenching strain depends on the dimensions of the sample used for quenching, crystals of the same dimensions (1 cm × 1 cm × 0·1 cm) were used in each case for thermal treatment. The heat treated samples were cleaved into three pieces and the interior and exterior pieces were separately X-irradiated for one hour under identical conditions of the X-ray tube. The X-rays with which the crystals were irradiated were obtained from a Philip's Micro-Apparatus Cu-target X-ray tubes operated at 30 KV and 10 mA. The samples were wrapped with black paper and were exposed to X-rays such that the large faces of the specimen were perpendicular to the X-ray beam about 2·0 cm from the tube window. X-ray irradiation was done for all the samples at room temperature ($\sim$30°C). To obtain uniform colouration, both the faces of the crystals were exposed, allowing each face to remain in the path of X-rays for half the total time of exposure.

2. Results and Discussion

The F bands in the different heat-treated samples together with that in an as grown crystal are shown in figures 1 and 2. It is seen that the F centre density in KCl crystals increases upon heat treatment. The increase is very large in crystals quenched in carbon tetrachloride compared to the increase in air-quenched crystals. The F bands formed in the outer region of the heat treated crystals are much stronger than the bands formed in the interior region. The height of the F band in the crystal slowly cooled in air is only slightly less than that in the crystal quenched in air. The increase in F band in the intrerior of the air quenched sample is very small while that of the crystal quenched in carbon tetrachloride is very large. The F centre concentration, n per c.c., has

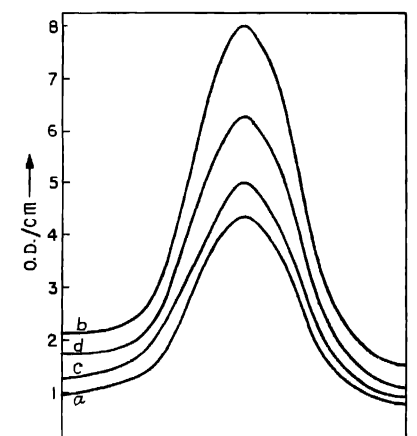

Fig. 1. F band absorptions in KCl crystals after heat treatment in air.

a) KCl, as grown, $n = 3{\cdot}5 \times 10^{16}$/c.c.

b) KCl, quenched and sample taken from the surface region, $n = 6{\cdot}2 \times 10^{16}$/c.c.

c) KCl, quenched and sample taken from the interior, $n = 3{\cdot}8 \times 10^{16}$/c.c.

d) KCl, slowly cooled, $n = 4{\cdot}9 \times 10^{16}$/c.c.

been measured in each case excluding the base absorption using Smakula's (Schulman & Compton 1962) formula and is shown in the figures.

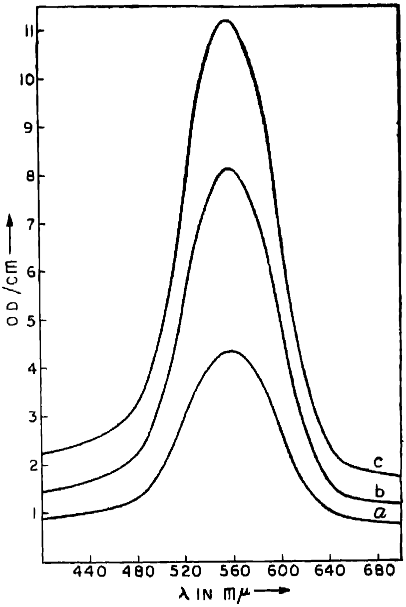

Figure 2 F band absorptions in KCl crystals after quenching in carbon-tetrachloride.
a) KCl, as grown, $n = 3\ 5 \times 10^{16}$/c.c.
b) KCl, quenched and sample taken from interior, $n = 6\ 8 \times 10^{16}$/c c
c) KCl, quenched and sample taken from surface region, $n = 9\ 2 \times 10^{16}$/c.c.

The measurements of hardness (Kear & Pratt 1959) and electrical conductivity (Bhuniya 1976) have shown that the concentration of thermally produced vacancies does not vary much from the interior to the outer region of the quenched crystal. But quenching strain differs very much being higher in the outer region. Again, increasing the quenching rate produces more distortion in the crystal *i.e.*, increases the severity of quenching stresses and strains. It also retains larger number of thermally produced vacancies in the crystal The higher concentration of F centres in the rapidly quenched crystal can be explained on the Hersh mechanism (Hersh 1966) of F centre formation. According to this mechanism a chlorine ion of the crystal during X-irradiation reduces to a neutral atom after losing an electron by the absorption of an X-ray photon. During subsequent relaxation the adjacent chlorine ion of the lattice moves towards the neutral atom and forms covalent bond with it producing a molecular chlorine ion (Cl_2^-). This in turn captures a moving electron from the conduction band forming a transitory molecule ($Cl_2^{=*}$) composed of an Cl_2^- centre containing an additional bound electron. These centres can also be produced when a chlorine ion of the crystal is excited during the process of irradiation, the excited ion forming covalent bond with the adjacent chlorine ion of the lattice. If this molecule is initially created or subsequently placed, in an excited vibronic, predissociative or repulsive state, it can dissociate into a normal chlorine ion and an uncaged chlorine atom moving into an interstitial position leaving behind a negative ion vacancy according to the reaction $Cl_2^{=*} \rightarrow Cl_2^{=**} \rightarrow Cl_{int} + \square + Cl^- + e$. Subsequent capture of electron by anion vacancy results in the formation of F centre. It can be stable only if the interstitial chlorine atom which have acquired sufficient kinetic energy in the dissociation process migrates away and relaxes in some positive ion vacancies or voids or grain boundaries leading to the formation of stable V centre (Christy & Phelps 1961). In the quenched crystal where the ions are already shifted from their normal lattice position because of quenching strain, comparatively less energy will be required for the formation of $Cl_2^{=*}$ molecules during X-radiation so that larger number of anion vacancies will be produced. These vacancies capture electrons and convert into stable F centres since the interstitial chlorine atoms after migration find large number of quenched in defects like vacancies, voids and grain boundaries where they relax and form stable V centres. So the larger number of F centres in rapidly quenched crystal is due to higher quenching strain and larger number of quenched in defects. The higher concentration of F centres in the outer region compared to interior region may be due to another reason over and above the higher quenching strain. Since the crystals are heated in air at 750°C for two hours before quenching, oxygen, hydroxyl and carbonate ions are present in the outer region of the quenched crystal (Kadorka & Vaske 1963) These ions enhance the F centre formation very much under X-irradiation (Frohlich & Grau 1965) Because of this region the height of the F band formed in the slowly cooled crystal which has been heated in air for a much longer time is only little less than that in the air-quenched crystal.

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